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Ion-Induced Nucleation in Polar Fluids

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極性流体の準安定気相における核生成率は、イオンが存在する場合は有意に促進される。我々は、イオン-極性分子間の静電相互作用による溶媒和効果や、イオン周囲における流体密度の不均一性を考慮したイオン誘起核生成理論を Ginzburg-Landau 理論に基づいて構築し、臨界液滴の生成エネルギーや密度分布を計算した。共存線上で、液相よりも気相の方が溶媒和エネルギーが大きく、その差が核生成障壁を低下させる要因となることを示す。

1 Introduction

It is well known that the nucleation rate in polar fluids is much enhanced due to the presence of ions [1,2]. The problem of heterogeneous nucleation triggered by ion-dipole interaction is of fundamental importance in physics and chemistry, but it has rarely been studied in the literature. We present a Ginzburg-Landau theory of ion-induced nucleation in polar one-component fluids in a gas phase. Our theory takes account of (i) *solvation* effect due to the electrostatic interaction between the ion and the polar solvent, and (ii) density inhomogeneity around the ion (*electrostriction*).

2 Ginzburg-Landau free energy

When an ion of charge Ze is placed at $\mathbf{r} = 0$ in a polar one-component fluid at uniform temperature T , the increment of the grand potential is written as

$$\Delta\Omega'[n] = \int d\mathbf{r} \left[g(n(\mathbf{r})) + \frac{C}{2} |\nabla n(\mathbf{r})|^2 + \frac{(Ze)^2 \theta^2(r)}{8\pi\epsilon(n(\mathbf{r}))r^4} + v_{\text{is}}(r)n(\mathbf{r}) \right], \quad (1)$$

with

$$g(n) = f(n) - f(n_\infty) - \mu_\infty(n - n_\infty). \quad (2)$$

Here, we assume that the density $n(\mathbf{r})$ tends to a homogeneous value n_∞ far from the ion ($r \rightarrow \infty$), and μ_∞ is the chemical potential. The Helmholtz free energy density $f(n)$ of the polar fluid is evaluated in the van der Waals theory. The coefficient C of the gradient term is chosen to reproduce the observed surface tension of the fluid. The potential $v_{\text{is}}(r)$ describes a short-range repulsive interaction between the ion and the solvent. We use the Harris-Alder formula for the static dielectric constant $\epsilon(n)$, which is an increasing function of the fluid density n for given T . The function $\theta(r) = [\min(r, R_i)/R_i]^3$ arises from the assumed uniform charge distribution inside the ion ($r < R_i$).

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3 Results

We determine the density profile $n(r)$ by requiring the extremum condition $\delta\Delta\Omega'[n]/\delta n = 0$. The stable solution of this equation gives the density profiles $n_g(r)$ in the gas phase and $n_\ell(r)$ in the liquid phase, whereas the unstable solution corresponds to the critical droplet profile, $n_{\text{cri}}(r)$. A numerical example of the density profiles for water is shown in Fig. 1(a) for $A \equiv 4(Ze)^2/27\pi\sigma k_B T_c = 50$ and $R_i/\sigma = 0.3$, where σ is the hard-core diameter of the water molecule and T_c is the critical temperature. The nucleation barrier W_c is evaluated as

$$W_c(\text{KO}) = \Delta\Omega'[n_{\text{cri}}] - \Delta\Omega'[n_g], \quad (3)$$

which is indicated by the dots (KO) in Fig. 1(b). When the critical droplet radius is much larger than the solvation shell radius, the KO result is close to the KO' approximation,

$$W_c(\text{KO}') = -\Delta_{\text{sol}} + W_c^0, \quad (4)$$

where $\Delta_{\text{sol}} = \Delta\Omega'[n_g] - \Delta\Omega'[n_\ell] (> 0)$ is the difference of solvation free energies in gas and in liquid, and W_c^0 is the nucleation free energy in the absence of ions or homogeneous nucleation. It is remarkable that the negative background $-\Delta_{\text{sol}}$ much favors nucleation around an ion in a metastable gas. The Thomson theory [2], which is based on macroscopic continuum electrostatics, gives larger nucleation rates in this example [dashed line in Fig. 1(b)].

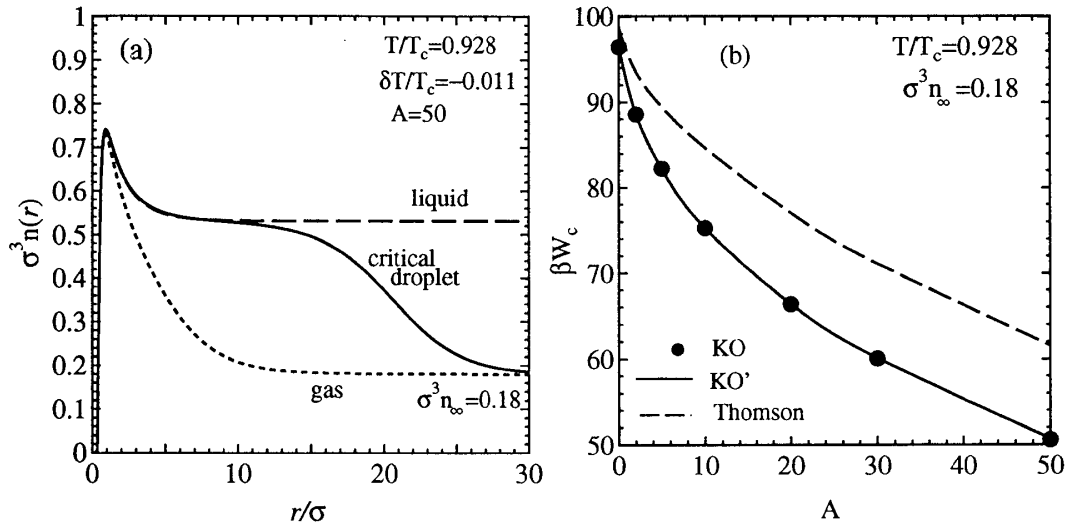


Figure 1: (a) Density profiles around an ion for $A = 50$. (b) Nucleation barrier ($\beta = 1/k_B T$).

References

- [1] C.T.R. Wilson, Phil. Trans. R. Soc. London Ser. A **189**, 265 (1897).
- [2] J.J. Thomson, *Conduction of Electricity through Gases* (Cambridge University Press, Cambridge, 1906), Sec.92.